

Magnetic studies on single crystals of a pseudo-tetrahedral nickel chelate, bis-isopropylsalicylaldiminato nickel(II)

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Magnetic studies on nickel (II) tetrahedral salts are rather meagre and these are mainly confined to the mean susceptibility measurements of powdered samples. The magnetic anisotropy in principal planes of single crystal of bis-isopropylsalicylaldiminato nickel (II) and mean magnetic susceptibility, in the temperature range 300°K-68°K, have been measured by us. Thermal behaviour of magnetic anisotropy indicates that orthorhombicity is substantial near 68°K though not so high near 300°K. This is in good agreement with the X-ray structural data on the salt. However, a detailed comparison on the basis of a tetragonal approximation, which may well prove useful for a first orientation, shows that the assumption of a negative value of Δ , the asymmetric field splitting parameter, for which a spin doublet level lies at about 72 cm^{-1} above the ground level, satisfying the experimental condition $K_{\perp} < K_{\parallel}$, (instead of a positive value), provides a much closer agreement of the experimental with the theoretical values of both mean susceptibilities and anisotropies.

INTRODUCTION

For a long time, apparent non-existence of tetrahedrally coordinated paramagnetic nickel (II) salts was generally assumed to be in accord with the simple crystal field theory (Bjerrum & Jorgensen 1956). However, Venanzi (1958) first reported the occurrence of tetrahedral Ni(II) complexes in salts of the type $(\text{Ph}_3\text{P})_2\text{NiX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I} \text{ \& \; NO}_3$) from X-ray structural study. Later, Gill & Nyholm (1959), Cotton & Goodgame (1960), Cotton *et al* (1961) and Goodgame *et al* (1961) have shown from X-ray and other physico-chemical studies that tetrahedral Ni(II) complexes could be formed with a variety of ligands. Magnetic studies of nickel (II) tetrahedral salts are very meagre and moreover, these are only confined to the mean susceptibility measurements of powdered samples (Gill & Nyholm 1959, Goodgame *et al* 1961, Cotton & Goodgame 1960, Cotton *et al* 1961, Sacconi *et al* 1963, 1964, 1965, Bose *et al* 1965).

Tetrahedrally coordinated Ni(II) compounds in the form of single crystals, other than cubic, of suitable size, will show magnetic anisotropy, so that the nature of the ligand field in these can be more effectively studied from thermal behaviour of both magnetic anisotropy and mean magnetic susceptibility. Fortunately, it is now definitely known from X-ray analysis of Sacconi *et al* (1962)

and Fox *et al* (1964) that nickel chelate compound bis-isopropylsalicylaldimine nickel(II) is tetrahedrally coordinated and belongs to the orthorhombic class. We have therefore taken up a thorough investigation of crystalline magnetic anisotropies and mean susceptibility of single crystals of this salt in the temperature range 300°K—68°K and have also attempted an analysis of these results in relation to the ligand field theory.

OPTICAL SPECTRAL STUDIES

The reflectance spectra of Ni(II)-bis-isopropyl salt as well as its absorption spectra in non-polar solvent by Sacconi *et al* (1963) reveal bands with maxima at 6.7, 10.9, 14.1, 16.9 and 19.6 kK and a shoulder near 9.5 kK ($1\text{kK} = 10^3\text{ cm}^{-1}$). Their assignments of the bands are based on the calculation of Liehr & Ballhausen (1959) and are as follows : The bands at 6.7 kK is identified with the spin-allowed transition ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and those at 14.1 kK and 16.9 kK with ${}^3T_1(F) \rightarrow {}^3T_1(P)$. The weak band at 10.9 kK is assigned to the spin-forbidden transition from the ground state 3T_1 to an upper state arising from 1D state of the free ion. The polarized single crystal spectra of some nickel chelates with derivatives of salicylaldehyde by Bose & Lin (1965) essentially resemble the observations of Sacconi *et al* (1963).

X-RAY CRYSTALLOGRAPHIC STUDIES

Sacconi *et al* (1962) first showed from powder diagrams and two dimensional Patterson synthesis that Ni^{2+} exhibits a tetrahedral coordination configuration, in Ni(II)-sal-isopropyl salt which is isomorphous with the cobalt(II) and zinc(II) analogues. Later on, Fox *et al* (1964) reported the details of three dimensional X-ray diffraction investigation of the structure. As revealed in their structural analysis, the coordination tetrahedron of the nickel chelate complex, having a pair each of oxygens and nitrogens, is considerably distorted and may be assumed to have orthorhombic symmetry. The interchelate angle between the planes, $\text{N}(1)-\text{Ni}-\text{O}(1)$ and $\text{N}(2)-\text{Ni}-\text{O}(2)$, which is a measure of the deviation from regular tetrahedron, is $81^\circ.5$ and the tetrahedron is squashed along the internal bisector of $\text{O}(1)-\text{Ni}-\text{O}(2)$ and $\text{N}(1)-\text{Ni}-\text{N}(2)$ (figure 1).

The crystals belong to the orthorhombic system (space group P_{bca}) with eight molecules in the unit cell and closest Ni-Ni distance is 7.66\AA . From the point of view of magnetic symmetry, only one pair of magnetically inequivalent complex exists in the unit cell. Since these are equally inclined with respect to crystallographic axes a , b and c , direction cosines of one will be the same in magnitude as those of the other but with opposite sign and as such they can be regarded as equivalent for the calculation of the ionic susceptibilities from crystalline ones.

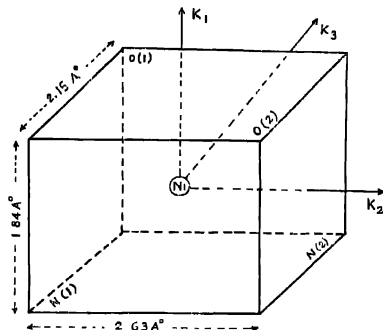


Figure 1. Showing principal ionic axes (K_1 , K_2 , K_3) and distortion of the ligand cluster of nickel(II) salicylaldimine.

SINGLE CRYSTAL PREPARATION AND EXTERNAL MORPHOLOGY OF SINGLE CRYSTAL

Single crystal of Ni(II)-bis-isopropylsalicylaldimine was prepared by refluxing bis-salicylaldehyde-nickel(II) dihydrate with a solution of amine in methanol and crystallized from cyclohexane. Fairly large dark brown crystals, with well developed faces (010), (001), usually elongated along the crystallographic c -axis, were obtained. The external morphology of the crystal is given in figure 2. The crystal axes have been identified by using goniometric and X-ray methods.

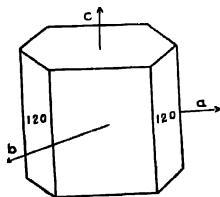


Figure 2. External morphology of a single crystal of nickel(II) salicylaldimine.

EXPERIMENTAL MEASUREMENTS OF PRINCIPAL CRYSTALLINE SUSCEPTIBILITIES (χ_a , χ_b , χ_c) AND CALCULATION OF PRINCIPAL IONIC SUSCEPTIBILITIES (K_1 , K_2 , K_3)

(a) Measurements of Crystalline Susceptibilities

The mean crystalline susceptibility ($\bar{\chi}$) and crystalline anisotropies in susceptibilities ($\chi_a - \chi_b$), ($\chi_c - \chi_a$) in (001) and (010) planes were measured in the temperature range 300°K—68°K using techniques described elsewhere (Guha Thakurta

& Mukhopadhyay 1966, Bose *et al* 1963). At room temperature the anisotropy in (100) plane i.e., $(\chi_b - \chi_c)$ was also determined to provide a check on the anisotropy measurements in (010) and (001) planes. It was established from the anisotropy measurements that $\chi_b > \chi_a > \chi_c$. The results are given in table 1. Also, in this table $T(\chi_b - \chi_a)$, $T(\chi_a - \chi_c)$ and \bar{P}^2 the mean square moment are included.

Table 1. Principal crystalline anisotropies, mean susceptibility, mean moment square etc. of Ni(II)-sal-isopropyl at different temperature

Temp. T °K	$(\chi_b - \chi_a)$ $\times 10^6$	$T(\chi_b - \chi_a)$ $\times 10^6$	$(\chi_a - \chi_c)$ $\times 10^6$	$T(\chi_a - \chi_c)$ $\times 10^6$	$\bar{\chi} \times 10^6$	\bar{P}^2
300	560.8	1682	370.1	1110	4587	11.00
280	603.0	1688	413.9	1159	4897	10.96
260	652.7	1697	465.6	1211	5255	10.92
240	713.4	1712	528.6	1269	5675	10.89
220	788.2	1734	602.7	1326	6171	10.85
200	883.8	1768	694.8	1390	6764	10.82
180	1012	1821	812.4	1462	7491	10.78
160	1187	1899	909.9	1552	8400	10.75
140	1417	1983	1190	1666	9557	10.70
120	1712	2054	1494	1793	11060	10.62
100	2116	2116	1901	1901	13040	10.43
80	2707	2166	2482	1985	15820	10.12
68	3223	2192	2981	2027	18150	9.86

(b) *Calculation of Ionic Susceptibilities :*

Since all the ions in the unit cell are in general position it is not possible to calculate the ionic susceptibilities K_1 , K_2 , K_3 , from the crystalline susceptibilities χ_a , χ_b , χ_c , alone even if we take ligand complexes to be approximately uniaxial, unless the orientations of the ion in the unit cell are known. In the absence of direct experimental evidences from EPR regarding the point group symmetry and orientation of the paramagnetic cluster, we have to fall back upon the X-ray values of the direction cosines of the geometric axes of the paramagnetic complex for the said purpose. With these data, the direction of K_1 was assumed to coincide with the mean direction of the two internal bisectors of the large angles [O(1)-Ni-O(2)] and [N(2)-Ni-N(1)] in the squashed tetrahedron, while those of K_2 and

K_3 to approximately coincide with the mean directions of other two pairs of internal bisectors of [O(1)-Ni-N(1)] and [O(2)-Ni-N(2)] and [O(2)-Ni-N(1)] and [O(1)-Ni-N(2)], respectively, so that K_1 , K_2 , K_3 form an orthorhombic set. The direction cosines of these ionic axes with respect to a , b , c , i.e., χ_a , χ_b , χ_c axes calculated from X-ray data are given below :

	$a(\chi_a)$	$b(\chi_b)$	$c(\chi_c)$
K_1	0.6608	0.2179	0.7182
K_2	0.1522	0.8993	-0.4078
K_3	0.7350	-0.3794	-0.5620

The principal ionic susceptibilities (K_1 , K_2 , K_3) at different temperatures are evaluated from crystalline susceptibilities (χ_a , χ_b , χ_c) by the use of the general relation :

$$\chi_i = \sum \lambda_{ji}^2 K_j, \quad (i = a, b, c; j = 1, 2, 3)$$

where λ_{ji} 's are the direction cosines between χ_i and K_j . Since, the structural data is available only at room temperature we assume in such calculation that the orientation of the paramagnetic cluster does not alter appreciably with change in temperature. The principal ionic susceptibilities so obtained are given in table 2.

Table 2. Ionic susceptibilities of Ni(II)-bis-isopropyl at different temperatures

Temperature °K	$K_1 \times 10^6$	$K_2 \times 10^6$	$K_3 \times 10^6$
300	2819	5878	5068
240	3232	7509	6288
200	3604	9168	7524
140	4229	13670	10780
100	4665	19610	14680
68	5085	28430	20930

The results indicate that the amount of ionic orthorhombicity present is quite substantial at 68°K though this is not so high at 300°K. This is also corroborated from the facts, namely, (a) the ionic anisotropies ($K_{\parallel} - K_{\perp}$) calculated from principal crystalline anisotropies ($\chi_b - \chi_a$) and ($\chi_a - \chi_c$) on the assumption of axial symmetry differ widely, progressively increasing with decreasing temperature

and (b) $(\chi_b - \chi_a)T$ and $(\chi_a - \chi_c)T$ vs temperature curves (figure 3) are quite distinct from each other.

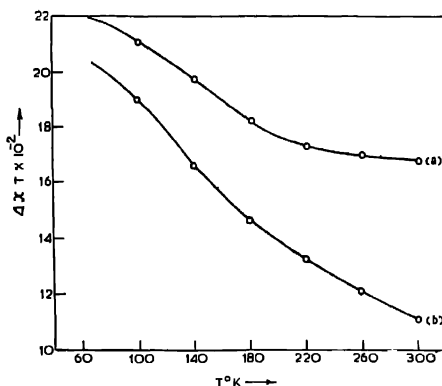


Figure 3. Temperature variation of $\Delta\chi.T$ in nickel(II) bis salicylaldehyde. (a) c axis vertical. (b) b axis vertical

DISCUSSION OF MEAN MOMENT AND ANISOTROPY IN MOMENT AND THEIR VARIATIONS WITH TEMPERATURE

The lowest configuration ($3d^8$) of a Ni^{2+} ion gives rise to terms 3F , 1D , 3P , 1G and 1S . Under the action of the tetrahedral cubic field, 3F ground term splits into ${}^3T_1(F)$, ${}^3T_2(F)$ and ${}^3A_2(F)$ in the ascending order of energy like $3d^2$ or $3d^7$ atomic system in an octahedral ligand distribution; while the same spin-multiplet term ${}^3T_1({}^3P)$, which is also important for magnetism since cubic field has matrix elements connecting ${}^3T_1(F)$ and ${}^3T_1(P)$, remains unsplit. Each of the orbital triplets will further split into a doublet and a singlet under lower symmetry tetragonal or trigonal field. These gross features of Stark pattern of Ni^{2+} in tetrahedral field is helpful for preliminary description of magnetic properties of nickel tetrahedral salts. The mean effective moment $\sqrt{P^2}$, of Ni-sal-isopropyl is 3.32 B.M. (spin only value is 2.83 B.M.) at 300°K, which is within the usual range of values (3.2-3.3 B.M.) for the distorted tetrahedral complexes of the type NiL_2X_2 (L = Ph_2P ; Miller 1962), but lower than the value 3.6-4.0 B.M. for the regular tetrahedral nickel(II) salts of the type $\text{R}_2[\text{NiX}_4]$, where R = $(\text{Et}_4\text{N})^+$ or $(\text{Ph}_3\text{MeAs})^+$ and X = Cl, Br, I (Gill & Nyholm 1959). Since for Ni^{2+} in a ligand field of tetrahedral symmetry, triplet ${}^3T_1(F)$ lies lowest, for which the orbital moment is non-zero, $\sqrt{P^2}$ depends substantially on the presence of low symmetry ligand field components as well as on electron delocalization. So, the low value for the present

crystal Ni(II)-bis-isopropyl indicates that the ligand field departs a good deal from regular tetrahedral symmetry. This is to be expected also from X-ray structural data showing a considerable departure from regular symmetry. Similar low value of $\sqrt{P^2}$ is also observed in octahedral nickel salts (2.9-3.2 B.M.), which however originates from an altogether different situation. In this case a non-magnetic orbital singlet A_{2g} is the ground state as a result of inversion of Stark pattern from the tetrahedral case, and in consequence the closeness of $\sqrt{P^2}$ to the spin-only value is essentially associated with the relative magnitudes of s.o. coupling and cubic field splitting.

It is to be generally expected, that the tetrahedrally co-ordinated paramagnetic complexes should resemble to some extent the octahedral complexes of the 'reciprocally related' (Van Vleck 1932) paramagnetic ions having similar Stark pattern. Thus like tetrahedral Ni^{2+} , octahedral V^{3+} and octahedral high spin Co^{2+} complexes have triplet states (${}^3T_1(F)$ and ${}^4T_1(F)$) lying lowest in cubic field. Of the two, V^{3+} octahedral complex is apparently more similar to Ni^{2+} tetrahedral, since the orbital as well as the spin degeneracies are the same for both. However, V^{3+} , and Ni^{2+} are actually very different in respect of both the magnitude and sign of cubic field coefficient as well as s.o. coupling [$D_q = 1894 \text{ cm}^{-1}$ and 372 cm^{-1} and $\lambda = +102$ and -325 cm^{-1} for V^{3+} octahedral and Ni^{2+} tetrahedral complexes, respectively] It will be then readily understood why for the V^{3+} octahedral the observed negative orbital contribution to the magnetic moment $\sqrt{P^2}$ is small compared to that of Ni^{2+} tetrahedral complex [1% and 15% for V^{3+} octahedral and Ni^{2+} tetrahedral complexes, respectively]. For octahedral Co^{2+} complexes, the cubic separation is only moderately large ($D_q = 1167 \text{ cm}^{-1}$) and s.o. coupling coefficient not too small ($\lambda = -180 \text{ cm}^{-1}$) like octahedral V^{3+} complexes. The percentage orbital contribution is quite large in most Co^{2+} complexes (about 22 per cent). This is mainly due to the facts that the splitting of the lowest triplet under rhombic field is only about 1000 cm^{-1} and mixing components under spin-orbit coupling are comparatively large and covalency effect possibly is less pronounced in Co^{2+} octahedral complexes.

The experimental \bar{P}^2 vs T curve of Ni-bis-isopropyl shown in figure 4 deviates from Curie law in a marked manner similar to octahedral Co^{2+} and V^{3+} complexes and very much unlike the octahedral Ni^{2+} complexes for which the magnetic moment is nearly independent of temperature. When we make a comparison of the ionic anisotropy in these complexes (on the simple assumption of axial symmetry), this is found to be much larger in Ni-bis-isopropyl than in V^{3+} octahedral complex and in even octahedral Co^{2+} complexes. The percentage anisotropy is about 58 at 300°K as against about 1.4 for $\text{V}(\text{KC}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ (Bose *et al* 1964) and nearly 44 for $\text{Co}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Guha Thakurta & Mukhopadhyay

1965). However, anisotropy behaviour in general is a more complicated function of structure and temperature, varying individually for different complexes of even

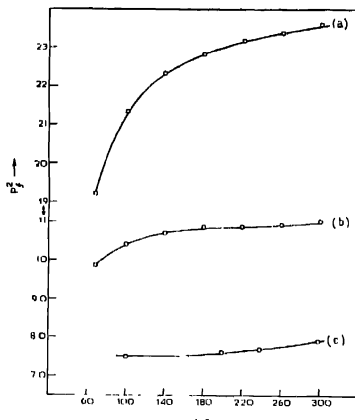


Figure 4. Temperature variation of mean square moments in (a) cobalt ammonium sulphate hexahydrate (Guha Thakurta & Mukhopadhyay 1966), (b) Ni(II) salicylaldimine (present author) (c) vanadium potassium oxalate (Bose *et al* 1964).

very similarly coordinated ion (44% and 31% for $\text{Co}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$, respectively, (Guha Thakurta & Mukhopadhyay 1965), and can be properly understood only after a close scrutiny of the minute details of the Stark patterns.

THEORETICAL CONSIDERATION OF MAGNETIC PROPERTIES OF PSEUDO-TETRAHEDRAL NICKEL(II) SYSTEM

Although magnetic data in conjunction with X-ray data offer enough indications for orthorhombicity of the ligand field, it is not so simple to deal with the orthorhombic model, because of too many parameters entering into the theory, and hence detailed comparison between experiment and theory becomes very difficult. So, in the theory which follows, we assume for simplicity a tetragonal distortion having D_{2d} symmetry and for the purpose of data fitting K_1 is equated to the average of K_2 and K_3 and $K_{||}$ to K_1 . Such a simplified picture may very well prove useful for a first orientation. The method of calculation has some similarity with those of Chakraborty (1959) and Bose *et al* (1964) for trigonally distorted octahedral vanadium alum and of Bose *et al* (1965) for trigonally distorted tetrahedral nickel salts. Although $3d^7 4p-3d^8$ configuration interaction is possible for

symmetry reasons, we have neglected this higher order effect for simplification in calculation.

The energies within the lowest orbital triplet ${}^3T_1(F)$ in cubic field may be calculated on the basis of Abragam & Pryce's theory (1951a) considering ${}^3T_1(F)$ as a pseudo- 3P -state. Then the elements of the Hamiltonian $H' = V_{tetragonal} - \alpha\zeta_{||}L_zS_z - \alpha'\zeta_{\perp}(L_xS_x + L_yS_y)$, comprising of the tetragonal component of the crystal field and s.o. coupling interaction (the reduction factor, due to charge cloud overlap, affects the free ion value of ζ in the crystal anisotropically, giving $\zeta_{||}$ and ζ_{\perp}), have to be evaluated within nine states $|m_l, m_s\rangle$ of a 3P term classified according to their values of $m = m_l + m_s$. The effect of the axial field is to split the triplet ${}^3T_1(F)$ into a doublet and a singlet having energies $-\Delta/3$ and $+2\Delta/3$, and whether doublet or the singlet lies lowest is determined by the sign of the axial field co-efficient Δ . The 9th order determinant corresponding to the Hamiltonian H' reduces according to the m values, into the following sub-determinants :

	$ -1, 1 \rangle$	$ 0, 0 \rangle$	$ 1, -1 \rangle$
$< -1, 1 $	$-\Delta/3 + \alpha\zeta_{ }$	$-\alpha'\zeta_{\perp}$	0
$< 0, 0 $	$-\alpha'\zeta_{\perp}$	$2\Delta/3$	$-\alpha'\zeta_{\perp}$
$< 1, -1 $	0	$-\alpha'\zeta_{\perp}$	$-\Delta/3$

$ 0, 1 \rangle$	$ 1, 0 \rangle$	$ -1, 0 \rangle$	$ 0, -1 \rangle$
$< 0, 1 $	$2\Delta/3$	$-\alpha'\zeta_{\perp}$	$< -1, 0 $
$< 1, 0 $	$-\alpha'\zeta_{\perp}$	$-\Delta/3$	$< 0, -1 $
	$-\alpha'\zeta_{\perp}$	$-\Delta/3$	$-\alpha\zeta_{ }$

$ 1, 1 \rangle$	$1, 1 $	$1, -1 $	$1, -1 $
$-\Delta/3 - \alpha\zeta_{ }$	$-\Delta/3 - \alpha\zeta_{ }$	$-\Delta/3 - \alpha\zeta_{ }$	$-\Delta/3 - \alpha\zeta_{ }$

The solutions of these are :

$$\begin{aligned}
 E_0 &= \frac{1}{2}[\Delta/3 + \alpha\zeta_{||} - S_0] \\
 E_1 &= \frac{1}{2}[\Delta/3 - S_1] \\
 E_2 &= [-\Delta/3 + \alpha\zeta_{||}] \\
 E_3 &= \frac{1}{2}[\Delta/3 + \alpha\zeta_{||} + S_0] \\
 E_4 &= \frac{1}{2}[\Delta/3 + S_1] \\
 E_5 &= [-\Delta/3 - \alpha\zeta_{||}]
 \end{aligned}$$

where $S_0 = [(\Delta - \alpha\zeta_{||})^2 + 8\alpha'^2\zeta_{\perp}^2]^{1/2}$ and $S_1 = [\Delta^2 + 4\alpha'^2\zeta_{\perp}^2]^{1/2}$

The corresponding wave functions obtained from the sets of secular equations are:

Eigen wavefunctions

$$\begin{aligned}
 \phi_0 &= a|1, -1\rangle + b|0, 0\rangle + a|-1, 1\rangle & m=0 \\
 \phi_1 &= c|1, 0\rangle + d|0, 1\rangle \\
 \phi_1' &= c|-1, 0\rangle + d|0, -1\rangle & m=\pm 1 \\
 \phi_2 &= -\frac{1}{\sqrt{2}}|-1, 1\rangle + \frac{1}{\sqrt{2}}|1, -1\rangle & m=0 \\
 \phi_3 &= \frac{b}{\sqrt{2}}|1, -1\rangle - \sqrt{2}a|0, 0\rangle + \frac{b}{\sqrt{2}}|-1, 1\rangle & m=0 \\
 \phi_4 &= d|1, 0\rangle - c|0, 1\rangle \\
 \phi_4' &= d|-1, 0\rangle - c|0, -1\rangle & m=\pm 1 \\
 \phi_5 &= |1, 1\rangle \\
 \phi_5' &= |-1, -1\rangle & m=\pm 2
 \end{aligned}$$

$$\text{where} \quad a = \frac{2\alpha'\zeta_{\perp}}{\alpha'\zeta_{\parallel} - \Delta + S_0} b; \quad 2a^2 + b^2 = 1$$

$$d = \frac{2\alpha'\zeta_{\perp}}{\Delta + S_1} c; \quad c^2 + d^2 = 1$$

Thus, under the action of an axial field and s.o. interaction the cubic ${}^3T_1(F)$ ground state splits into six levels, namely, three non-magnetic singlets and three magnetic doublets. The sequence of energy levels for positive and negative Δ 's (for reasonable values of parameters $\alpha'\zeta_{\parallel}$ and $\alpha'\zeta_{\perp}$) are shown in figure 5.

PRINCIPAL MAGNETIC SUSCEPTIBILITIES

With the wave functions for the nine states, the principal gm. ionic susceptibilities have been calculated by means of the standard procedure (Van Vleck 1932).

The magnetic operators acting on the ligand field $H_{m\parallel} = -\beta H\{\alpha k_{\parallel}L_z + 2S_z\}$ for magnetic field $H\parallel$ to the tetragonal axis of magnetic complex, and $H_{m\perp} = \beta H\{(-\alpha'k_{\perp}/2)(L_+ + L_-) + S_+ + S_-\}$ for H_{\perp} to tetragonal axis of magnetic complex.

In the above the effects of the overlap of d -wavefunctions with ligand wavefunctions are taken care of by the anisotropic orbital reduction factors k_{\parallel} , k_{\perp} .

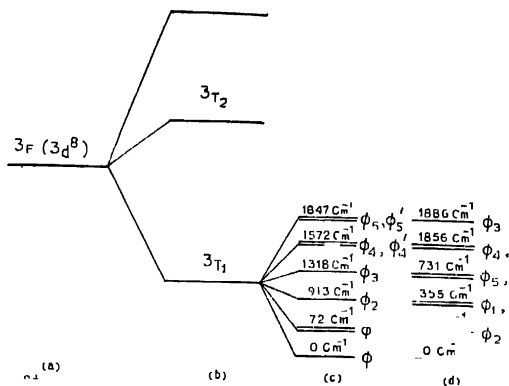


Figure 5. Fine structure energy level schemes for nickel(II) salicylaldimino (not to scale) (a) the free ion; (b) tetrahedral field, T_d ; (c) T_d + tetragonal component + s.o interaction ($\Delta = -1400 \text{ cm}^{-1}$, $\alpha\zeta_{||} = -325 \text{ cm}^{-1}$, $\alpha'\zeta_{\perp} = -270 \text{ cm}^{-1}$); (d) T_d + tetragonal component + s.o interaction ($\Delta = +1400 \text{ cm}^{-1}$, $\alpha\zeta_{||} = -325 \text{ cm}^{-1}$, $\alpha'\zeta_{\perp} = -270 \text{ cm}^{-1}$).

The anisotropic spin orbit reduction factors have been already included in ζ to make it $\zeta_{||}$, ζ_{\perp} . The expressions for $K_{||}$ and K_{\perp} are obtained as given below :

$$K_{||} = \frac{N\beta^2}{Zk} \left\{ \frac{1}{T} \{ G_{1z} E_1 e - E_1/kT + G_{1z} E_4 e - E_4/kT + G_{1z} E_5 e - E_5/kT \} + 2k \{ G_{2z} E_0 e - E_0/kT \right. \\ \left. + G_{2z} E_1 e - E_1/kT + G_{2z} E_2 e - E_2/kT + G_{2z} E_3 e - E_3/kT + G_{2z} E_4 e - E_4/kT \} \right\},$$

$$K_{\perp} = \frac{2N\beta^2}{Z} \left\{ G_{2x} E_0 e - E_0/kT + G_{2x} E_1 e - E_1/kT + G_{2x} E_2 e - E_2/kT + G_{2x} E_3 e - E_3/kT \right. \\ \left. + G_{2x} E_4 e - E_4/kT + G_{2x} E_5 e - E_5/kT \right\},$$

where G_1 and G_2 are the first and second order Zeeman terms and Z is the partition function given by

$$Z = e^{-E_0/kT} + 2e^{-E_1/kT} + e^{-E_2/kT} + e^{-E_3/kT} + 2e^{-E_4/kT} + 2e^{-E_5/kT}$$

The expressions for G 's are as follows :

$$G_{1z} E_1 = 2 \{ \langle \phi_1 | H_{m||} | \phi_1 \rangle \}^2 = 2 \{ (2d^2 - \alpha k_{||} c^2) + (d\nu_1 + 1) \}^2$$

$$G_{1z} E_4 = 2 \{ \langle \phi_4 | H_{m||} | \phi_4 \rangle \}^2 = 2 [2c^2 - \alpha k_{||} d^2]^2$$

$$\begin{aligned}
G_{1z}^{E_5} &= 2\{ \langle \phi_5 | H_{m||} | \phi_5 \rangle \}^2 = 2[\alpha k_{||} - 2]^2 \\
G_{2z}^{E_0} &= | \langle \phi_0 | H_{m||} | \phi_2 \rangle |^2, \quad G_{2z}^{E_1} = \frac{2 | \langle \phi_1 | H_{m||} | \phi_4 \rangle |}{E_4 - E_1} \\
G_{2z}^{E_2} &= \frac{| \langle \phi_2 | H_{m||} | \phi_0 \rangle |^2}{E_0 - E_2} + \frac{| \langle \phi_2 | H_{m||} | \phi_3 \rangle |^2}{E_3 - E_2} \\
G_{2z}^{E_3} &= \frac{| \langle \phi_3 | H_{m||} | \phi_2 \rangle |^2}{E_2 - E_3}, \quad G_{2z}^{E_4} = \frac{2 | \langle \phi_4 | H_{m||} | \phi_1 \rangle |^2}{E_1 - E_4}
\end{aligned}$$

where

$$\begin{aligned}
| \langle \phi_0 | H_{m||} | \phi_2 \rangle |^2 &= 2\alpha^2(\alpha k_{||} + 2)^2 \\
| \langle \phi_1 | H_{m||} | \phi_4 \rangle |^2 &= c^2 d^2 (\alpha k_{||} + 2)^2 \\
| \langle \phi_2 | H_{m||} | \phi_3 \rangle |^2 &= b^2 (\alpha k_{||} + 2)^2
\end{aligned}$$

$$\begin{aligned}
G_{2x}^{E_0} &= \frac{2A_1}{E_1 - E_0} + \frac{2A_2}{E_4 - E_0} \\
G_{2x}^{E_1} &= \frac{2A_1^2}{E_0 - E_1} + \frac{2A_3^2}{E_2 - E_1} + \frac{2A_4^2}{E_3 - E_1} + \frac{2A_5^2}{E_6 - E_1} \\
G_{2x}^{E_2} &= \frac{2A_5^2}{E_1 - E_2} + \frac{2A_6^2}{E_4 - E_2} \\
G_{2x}^{E_3} &= \frac{2A_4^2}{E_1 - E_3} + \frac{2A_7^2}{E_4 - E_3} \\
G_{2x}^{E_4} &= \frac{2A_2^2}{E_0 - E_4} + \frac{2A_6^2}{E_2 - E_4} + \frac{2A_7^2}{E_3 - E_4} + \frac{2A_8^2}{E_5 - E_4} \\
G_{2x}^{E_5} &= \frac{2A_5^2}{E_1 - E_5} + \frac{2A_8^2}{E_4 - E_5}
\end{aligned}$$

where

$$\begin{aligned}
A_1 &= \sqrt{2}\{ac + bd - \tfrac{1}{2}\alpha'k_1bc - \tfrac{1}{2}\alpha'k_1ad\} + \sqrt{2}\{ac\nu_2 + ad\nu_3 + bd\nu_4\} \\
A_2 &= \sqrt{2}\{ad - bc + \tfrac{1}{2}\alpha'k_1ac - \tfrac{1}{2}\alpha'k_1bd\} \\
A_3 &= \{c + \tfrac{1}{2}\alpha'k_1d\} \\
A_4 &= \{bc - 2ad + \alpha'k_1ac - \tfrac{1}{2}\alpha'k_1bd\} \\
A_5 &= \sqrt{2}\{c - \tfrac{1}{2}\alpha'k_1d\} \\
A_6 &= \{d - \tfrac{1}{2}\alpha'k_1c\} \\
A_7 &= \{bd + 2ac + \alpha'k_1ad + \tfrac{1}{2}\alpha'k_1bc\} \\
A_8 &= \sqrt{2}\{d + \tfrac{1}{2}\alpha'k_1c\}
\end{aligned}$$

In the expressions for $G_{1z}^{B_1}$ and A , terms containing ν 's are the contributions from upper 3P levels, coming directly through the lowest ϕ_0 , calculated in the manner of Abragam & Pryce (1951b), where

$$\begin{aligned}\nu_1 &= -\zeta \left(\frac{2q_1q_2}{\pi_{xy}} - \frac{15f_1f_2}{2\psi_{xy}} \right), & \nu_3 &= -\zeta \left(\frac{15f_1f_2}{8\psi_{xy}} - \frac{q_1q_2}{2\pi_{xy}} \right), \\ \nu_2 &= -\zeta \left(\frac{15}{8} \frac{f_2^2}{\psi_z} + \frac{2\zeta^2}{\chi} + \frac{3}{2} \frac{q_2^2}{\pi_z} \right), & \nu_4 &= -\zeta \left(\frac{15}{4} \frac{f_2^2}{\psi_{xy}} + \frac{q_2^2}{\pi_{xy}} \right),\end{aligned}$$

symbols having the meaning given in the above reference.

As mentioned in the previous section, the lowest level has been shown to be a spin singlet ϕ_0 and from our parametral fitting of experimental data of magnetic susceptibility and anisotropy as given later, it comes out that the next level lying at about 72 cm^{-1} above the ground spin singlet ϕ_0 is the spin doublet (ϕ_1, ϕ_1') . As the population density of the doublet ϕ_1, ϕ_1' is appreciable at ordinary temperatures ($kT \approx 200 \text{ cm}^{-1}$), EPR signal, if any, may be observed only for this level, with effective spin = $1/2$, and the g -factors will be given by

$$\begin{aligned}g_{||} &= \langle \phi_1 | -\alpha k_{||} L_z + 2S_z | \phi_1 \rangle = 2[2d^2 - \alpha k_{||} c^2] \\ g_{\perp} &= \langle \phi_1 | -\alpha' k_{\perp} L_x + 2S_x | \phi_0 \rangle = 0\end{aligned}$$

However, the intensity of the resonance signal corresponding to $g_{||}$ may not be appreciable to be observed, since it is proportional to g_{\perp}^2 which is zero in the first order and in fact, no EPR signal has been detected at X-band.

ESTIMATION OF PHYSICAL PARAMETERS FROM FITTING OF EXPERIMENTAL DATA FOR MAGNETIC ANISOTROPY AND MEAN SUSCEPTIBILITY AT VARIOUS TEMPERATURES

The theoretical expressions for the ionic susceptibilities are functions of five parameters viz. $\alpha\zeta_{||}$, $\alpha'\zeta_{\perp}$, $\alpha k_{||}\alpha'k_{\perp}$ and Δ . Then the correlation of the experimentally obtained principal ionic susceptibilities with the theoretical ones may be obtained with the data at any three temperatures (provided both mean susceptibility and anisotropy data are available), to decide the values of these parameters uniquely, assuming these to be temperature independent. It is, however, likely that some of the field parameters are fairly sensitive to changes of temperature. On the other hand, all the parameters are not explicitly independent of one another, and may be related to the anisotropic field parameter Δ , but it is difficult to get the actual relationship between them. Then it is in theory possible to calculate the parameters, assuming a varying Δ with temperature. From the physical standpoint we shall be thus putting the sole responsibility of the thermal dependence of all the parameters on Δ which though perhaps a somewhat exaggerated

picture, gives some idea of the behaviours of the ligand field. For the present salt, it is found that no single set of parameters ($\alpha'\zeta_{||}$, $\alpha'\zeta_{\perp}$, $\alpha'k_{||}$, $\alpha'k_{\perp}$ and Δ) can bring the data fitting with the theory within the limit of experimental errors at all temperatures. But since we have already made the approximate assumption of axial symmetry instead of the more correct orthorhombic symmetry and moreover we have taken for granted that the paramagnetic clusters do not rotate with temperatures *i.e.*, the direction cosines λ_H remain unaltered with temperature, it appears superfluous to arrive at a *very close fit* with the experimental values at all temperatures by changing Δ with temperature. It would be of course possible to exactly fit the data at any three temperatures, taking Δ to be independent of temperature. But the fitting at other temperatures will be bad. So, we have attempted *only* to find out the set of values of the parameters, which give the closest approach within experimental errors with the observed susceptibilities at room temperature, which is always treated as standard, and keep the deviations at the minimum at other temperatures. The sequence of the fine structure energy levels and their separations, in cm^{-1} for positive and negative values of Δ (for reasonable values of parameters $\alpha'\zeta_{||}$ and $\alpha'\zeta_{\perp}$) are shown in figures 5a and 5b. In both cases the lowest level has been shown to be a spin singlet ϕ_0 while the next higher state is a doublet (ϕ_1, ϕ_1') for negative Δ and a singlet ϕ_2 for positive Δ . Consequently the effective magnetic moment should be comparatively smaller in the latter case and it has been found on actual calculation that the effective magnetic moment in that case (*i.e.* positive Δ) practically comprises of second

Table 3 Results of closest fitting of experimental mean susceptibility and anisotropy at different temperatures with the most representative set of theoretical parameters

$$\begin{aligned} \alpha'\zeta_{||} &= -325 \text{ cm}^{-1} & \alpha'\zeta_{\perp} &= -270 \text{ cm}^{-1} \\ \alpha'k_{||} &= 1.00 & \alpha'k_{\perp} &= 1.18 \\ \Delta &= -1400 \text{ cm}^{-1} \end{aligned}$$

Temperature °K	$(K_{\perp} - K_{ }) \times 10^6$		$\bar{K} \times 10^6$	
	Expt.	Theo.	Expt.	Theo.
300	2654	2641	4587	4615
240	3667	3417	5675	5682
200	4742	4258	6764	6743
140	7997	6681	9557	9419
100	12570	10360	13040	12800
68	19600	16920	18150	17640

order contributions and much smaller than that experimentally obtained. Moreover, for positive Δ , K_{\parallel} comes out to be greater than K_{\perp} in direct contradiction with the experimental results. For negative value of Δ , the rest of the levels other than (ϕ_1, ϕ_1') are well separated from ϕ_0 ($\approx 1200 \text{ cm}^{-1}$) and the orbital contributions to both K_{\parallel} and K_{\perp} are primarily dictated by the doublet (ϕ_1, ϕ_1') in the first and second order, respectively. Although some discrepancies (rather pronounced in anisotropy) have been noted at low temperatures, the negative Δ consideration provides closer agreements of the theoretical values of both mean susceptibilities and anisotropies and satisfies the experimental condition $K_{\perp} > K_{\parallel}$. The results of best fitting of experimental mean susceptibility and anisotropy (not so good) obtained with negative Δ are shown in table 3.

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